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## (54) LITHIUM SECONDARY BATTERY

## (57)Abstract:

PROBLEM TO BE SOLVED: To improve charge/discharge cycle characteristics and suppress lowering of battery capacity, by using, as a positive-electrode active material, a  $\text{LiMn}_2\text{O}_4$  spinel with Mn partly substituted with two elements, Li and Cr, simultaneously, thereby improving elution of Mn into a nonaqueous electrolyte and reversibility following charge/discharge, of crystal structure of the positive-electrode active material.

SOLUTION: A compound for a positive-electrode active material is expressed by an expression,  $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$ . (In the expression, a: the amount of Li substituted, b: the amount of Cr substituted.) It is preferable to cause the a and b to satisfy,  $0.01 \leq a+b \leq 0.5$ , and especially,  $0.15 \leq a+b \leq 0.3$ , and  $a \neq 0$ ,  $b \neq 0$ , whereby an Mn elution suppressing effect is maximized and no different phases are generated making no contribution to battery reaction. The crystal structure of this compound has flexibility with respect to insertion/desorption of Li ions. This compound is suitably obtained as a single phase, by firing a mixture made by mixing, at a fixed ratio, salts, such as carbonates and acetates, of respective elements, not generating harmful decomposition gases, with an oxide, in an oxidizing atmosphere at 700 to 900° C for 5 to 50 hours.

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(54) 【発明の名称】 リチウム二次電池

(57) 【要約】

【課題】 リチウム遷移金属複合酸化物を正極活物質として用いた充放電サイクル特性の良好なリチウム二次電池を提供する。

【解決手段】 正極活物質として用いる  $\text{LiMn}_2\text{O}_4$  スピネルの Mn の一部を Li および Cr の2元素で同時置換する。

## 【特許請求の範囲】

【請求項 1】  $\text{LiMn}_2\text{O}_4$  スピネルの Mn の一部を、Li および Cr の 2 元素で同時置換した Li ( $\text{Li}_a\text{Cr}_b$ )  $\text{Mn}_{2-(a+b)}\text{O}_4$  (但し、a は Li 置換量、b は Cr 置換量を表す。) を正極活物質として用いたことを特徴とするリチウム二次電池。

【請求項 2】 当該置換量 a、b が、 $0.01 \leq a+b \leq 0.5$ 、 $a \neq 0$ 、 $b \neq 0$ 、の関係を満足することを特徴とする請求項 1 記載のリチウム二次電池。

【請求項 3】 当該置換量 a、b が、 $0.15 \leq a+b \leq 0.3$ 、 $a \neq 0$ 、 $b \neq 0$ 、の関係を満足することを特徴とする請求項 2 記載のリチウム二次電池。

【請求項 4】 当該 Li ( $\text{Li}_a\text{Cr}_b$ )  $\text{Mn}_{2-(a+b)}\text{O}_4$  が、所定比に調整された各元素の塩および/または酸化物の混合物を、酸化雰囲気、 $700^\circ\text{C} \sim 900^\circ\text{C}$  の範囲で、5 時間～50 時間かけて焼成し、得られたものであることを特徴とする請求項 1～3 のいずれか一項に記載のリチウム二次電池。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、携帯型電子機器の作動電源、電気自動車あるいはハイブリッド電気自動車等のモータ駆動電源として使用される二次電池の中で、リチウム遷移金属複合酸化物を正極活物質として用いた、充放電サイクル特性の良好なリチウム二次電池に関する。

## 【0002】

【従来の技術】 近年、携帯電話、VTR、ノート型コンピュータ等の携帯型電子機器の小型軽量化が加速度的に進行しており、その電源用電池としては、正極活物質にリチウム複合酸化物を、負極活物質に炭素質材料を、電解液に Li イオン電解質を有機溶媒に溶解した有機電解液を用いた二次電池が用いられるようになってきている。

【0003】 このような電池は、一般的にリチウム二次電池、もしくはリチウムイオン電池と称せられており、エネルギー密度が大きく、また単電池電圧も約 4 V 程度と高い特徴を有することから、前記携帯型電子機器のみならず、最近の環境問題を背景に、低公害車として積極的な一般への普及が図られている電気自動車あるいはハイブリッド電気自動車のモータ駆動電源としても注目を集めている。

【0004】 このようなリチウム二次電池においては、その電池容量や充放電サイクル特性（以下、「サイクル特性」という。）は、使用する正極活物質の材料特性に依存するところが多い。正極活物質としてのリチウム遷移金属複合酸化物としては、具体的に、 $\text{LiCoO}_2$ 、 $\text{LiMn}_2\text{O}_4$  等が用いられているが、 $\text{LiCoO}_2$  については、Co の産出地が限られており、また産出量が決して多いとは言えず高価であるため、汎用的なリチ

ウム二次電池に用いるには問題がある。また、 $\text{LiMn}_2\text{O}_4$  と比較すると出力密度が小さいという問題もある。

【0005】 一方、 $\text{LiMn}_2\text{O}_4$  は、原料が安価であり、また、出力密度が大きく、電位が高いという特徴がある。しかしながら、 $\text{LiMn}_2\text{O}_4$  を正極活物質として用いた場合には、充放電サイクルの繰返しに伴って徐々に放電容量が低下し、良好なサイクル特性が得られないという問題がある。これは  $\text{Li}^+$  の挿入・脱離によって結晶構造が非可逆的に変化することによるものと考えられている。

【0006】 そこで、この結晶構造の可逆性を改善するため、 $\text{LiMn}_2\text{O}_4$  の骨格に他の元素を固溶させる、つまり、Mn の一部を他の一元素で置換することが有効であるとの報告がされており、 $\text{Mn}^{3+}$  と同じ +3 価イオン、たとえば Co、Fe、Cr 等による元素置換が検討されている。

## 【0007】

【発明が解決しようとする課題】 このような +3 価イオンによる元素置換を行うことにより、元素置換前よりもサイクル特性が向上することは事実であり、したがって、 $\text{Li}^+$  の挿入・脱離に伴う結晶構造の可逆性の改善が図られていると考えられる。しかしながら、発明者らは、このような元素置換したスピネルを正極材料として用いた場合であっても、サイクル運転を行うと、経時的に、電解液として使用される非水電解液中への Mn の溶出が起こり、この Mn の溶出もまた、正極容量（電池容量）の低下の原因となっており、サイクル特性が低下するものと考えた。

【0008】 したがって、電池のサイクル特性を向上させるには、 $\text{Li}^+$  の挿入・脱離に対するフレキシビリティを有する結晶構造を有するのみならず、同時に非水電解液との化学的反応性が抑えられたスピネル、好ましくは Mn の溶出が全く起こらないスピネルを、正極活物質として用いることが好ましい。

## 【0009】

【課題を解決するための手段】 本発明は、上述した従来技術の問題点に鑑みてなされたものである。すなわち、本発明によれば、 $\text{LiMn}_2\text{O}_4$  スピネルの Mn の一部を、Li および Cr の 2 元素で同時置換した Li ( $\text{Li}_a\text{Cr}_b$ )  $\text{Mn}_{2-(a+b)}\text{O}_4$  (但し、a は Li 置換量、b は Cr 置換量を表す。) を正極活物質として用いたことを特徴とするリチウム二次電池、が提供される。

【0010】 ここで、Li 置換量 a、Cr 置換量 b は、 $0.01 \leq a+b \leq 0.5$ 、 $a \neq 0$ 、 $b \neq 0$ 、の関係を同時に満足していることが好ましい。また、置換量 a、b が、 $0.15 \leq a+b \leq 0.3$ 、 $a \neq 0$ 、 $b \neq 0$ 、の範囲にあることが、さらに好ましい。なお、この Li ( $\text{Li}_a\text{Cr}_b$ )  $\text{Mn}_{2-(a+b)}\text{O}_4$  の合成は、好適には、所定比に調整された各元素の塩および/または酸化物の混合物を、酸化雰囲気、 $700^\circ\text{C} \sim 900^\circ\text{C}$  の範囲

で、5時間～50時間かけて焼成することで行われる。

【0011】

【発明の実施の形態】 本発明のリチウム二次電池においては、 $\text{Li}^+$ の挿入・脱離に対する結晶構造の可逆性を改善してサイクル特性を向上させると同時に、 $\text{Mn}$ の非水電解液への溶出を抑制することによっても、正極容量の低下を抑制してサイクル特性を向上させるために、 $\text{LiMn}_2\text{O}_4$ スピネルの $\text{Mn}$ の一部を、 $\text{Li}$ および $\text{Cr}$ の2元素で同時置換した $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$ （但し、 $a$ は $\text{Li}$ 置換量、 $b$ は $\text{Cr}$ 置換量を表す。）を正極活物質として用いる。

【0012】 全体の置換量（以下、「全置換量」という。） $a+b$ は、 $0.01 \leq a+b \leq 0.5$ の範囲とされ、ここで、 $\text{Li}$ と $\text{Cr}$ の個々の置換量 $a$ 、 $b$ は、 $a \neq 0$ 、 $b \neq 0$ の条件を同時に満たす必要がある。すなわち、 $\text{Mn}$ の非水電解液への溶出を抑制するためには、 $\text{Li}$ と $\text{Cr}$ の2元素を一对とした同時置換が必要であり、いずれか一方の元素が欠けても、 $\text{Mn}$ 溶出を抑える効果を発揮することができない。そして、全置換量 $a+b$ が、 $0.15 \leq a+b \leq 0.3$ の範囲にあるとき、後述する実施例に示されるように、最も $\text{Mn}$ の溶出抑制効果が発揮され、良好なサイクル特性が得られる。

【0013】 なお、全置換量 $a+b$ が0.01以下では、サイクル特性の向上が現れず、同時置換の効果が認められない。一方、全置換量 $a+b$ が0.5超では、材料合成において異相の生成が粉末X線回折法（XRD）により認められ、すなわち、単相物質が得られない。このような異相は、正極活物質の重量を増すだけで電池反応には寄与しないことから、その生成を避けなければならないことはいうまでもない。

【0014】 上述した $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$ を正極活物質として用いることにより、 $\text{Li}^+$ の挿入・脱離に対する結晶構造の可逆性の改善および $\text{Mn}$ の非水電解液への溶出の抑制が同時に図られ、サイクル特性の飛躍的な向上が図られる。このようなサイクル特性の向上は、特に電気自動車やハイブリッド電気自動車のモータ駆動用電源として用いた場合には、所定の加速性能、登坂性能といった走行性能を維持し、また、一充電当たりの継続走行距離を維持するために極めて重要である。

【0015】  $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$ の作製は、原料として所定比に調整された各元素の塩および／または酸化物の混合物を、酸化雰囲気、 $700^\circ\text{C} \sim 900^\circ\text{C}$ の範囲で、5時間～50時間かけて焼成することで行われ、こうして単相の生成物を得ることができる。

【0016】 ここで、各元素の塩は特に限定されるものではないが、原料として純度が高くしかも安価なものを使用することができることが好ましいことはいうまでもなく、昇温、焼成時に有害な分解ガスが発生しない炭酸塩、酢酸塩を用いることが好ましいが、硝酸塩や塩酸

塩、硫酸塩等を用いることもできる。

【0017】 さて、電池の作製に当たって使用される他の材料は、特に限定されるものではなく、従来公知の種々の材料を用いることができる。たとえば、負極活物質としては、ソフトカーボンやハードカーボンといったアモルファス系炭素質材料や高黒鉛化炭素材料等の人造黒鉛、あるいは天然黒鉛といった炭素質材料を用いることができる。

【0018】 また、有機電解液としては、エチレンカーボネート（EC）、ジエチルカーボネート（DEC）、ジメチルカーボネート（DMC）といった炭酸エステル系のもの、プロピレンカーボネート（PC）やγ-ブチロラクトン、テトラヒドロフラン、アセトニトリル等の有機溶媒の単独溶媒もしくは混合溶媒に、電解質としての $\text{LiPF}_6$ や $\text{LiBF}_4$ 等のリチウム錯体フッ素化合物、あるいは $\text{LiClO}_4$ といったリチウムハロゲン化物等を1種類もしくは2種類以上を溶解したものが好適に用いられる。

【0019】

【実施例】 以下、本発明を実施例に実験結果に基づき更に詳細に説明する。

【0020】 （正極活物質 $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$ の製造）出発原料として、市販の $\text{Li}_2\text{CO}_3$ 、 $\text{MnO}_2$ 、 $\text{Cr}_2\text{O}_3$ の各粉末を用い、表1の左欄に示す各種の組成となるように秤量、混合し、酸化雰囲気、 $800^\circ\text{C}$ で24時間焼成し、正極活物質を合成した。ここで、比較のために、 $\text{Mn}$ の一部を $\text{Li}$ のみ、または $\text{Cr}$ のみで置換した材料、および置換を行わない $\text{LiMn}_2\text{O}_4$ も合成した。なお、元素置換を行わない $\text{LiMn}_2\text{O}_4$ を除き、全置換量 $a+b$ は、全て0.15とした。

【0021】

【表1】

	正極活物質組成	$\text{Mn}$ 量( $10^{-3}\text{mol/L}$ )
実施例1	$\text{Li}(\text{LiCr})_{0.15}\text{Mn}_{1.85}\text{O}_4$	<0.1
比較例1	$\text{LiLi}_{0.15}\text{Mn}_{1.85}\text{O}_4$	4
比較例2	$\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$	3
比較例3	$\text{LiMn}_2\text{O}_4$	12

【0022】 （電池の製造）まず、上述の通りにして作製した種々の正極活物質のそれぞれについて、正極活物質と、導電材たるアセチレンブラック粉末と、結着材たるポリフッ化ビニリデンを、重量比で5:0:2:3の比で混合し、正極材料を作製した。その正極材料0.02gを $300\text{kg}/\text{cm}^2$ の圧力で直径20mmφの円板状にプレス成形し、正極とした。こうして作製した正極と、エチレンカーボネートとジエチルカーボネートが等体積比で混合された有機溶媒に電解質としての $\text{LiPF}_6$ を $1\text{mol/L}$ なる割合で溶解した電解液と、カーボンからなる負極、および正極と負極を隔てるセパレー

タとを用いて、コインセルを作製した。

【0023】（正極活物質の非水電解液中への溶出量の測定）作製したコインセルを正極活物質の容量に応じて1Cレートの定電流-定電圧で4.1Vまで充電し、同じく1Cレートの定電流で2.5Vまで放電させる充放電試験を100サイクル行った後、コインセルから非水電解液を抽出し、蒸留水で100倍に希釈した後、非水電解液中に含まれるMn量を誘導結合高周波プラズマ発光装置（ICP）を用いて分析した。電池製造時の非水電解液にはMnは含まれていないため、この分析により、正極活物質からのMnの溶出の度合いを知ることができる。

【0024】ICPの測定結果を表1の右欄に記す。元素置換を行わない $\text{LiMn}_2\text{O}_4$ と比較して、LiまたはCrのいずれか一方による置換を行ったものでは、Mnの溶出量が1/3～1/4程度に抑えられているに止まっているが、LiおよびCrの2元素による同時置換を行った本発明の $\text{Li}(\text{LiCr})_{0.15}\text{Mn}_{1.85}\text{O}_4$ では、Mnの溶出がほとんど完全に抑制されていることがわかる。つまり、Mnの溶出を抑制するためには、MnのLiまたはCrのいずれか一方による置換では不十分であり、LiおよびCrの2元素による同時置換により、初めてほぼ完全にMnの溶出を抑制することが可能となった。

【0025】次に、LiおよびCrの2元素による同時置換において、Mn溶出抑制効果が得られる全置換量 $a+b$ の範囲を調べた。合成した正極活物質の組成と、上述したICPを用いた分析によるMn溶出量の測定結果を表2に示す。

【0026】

【表2】

	正極活物質組成	Mn量( $10^{-3}\text{mol/L}$ )
比較例4	$\text{Li}(\text{LiCr})_{0.008}\text{Mn}_{1.992}\text{O}_4$	3
実施例2	$\text{Li}(\text{LiCr})_{0.01}\text{Mn}_{1.99}\text{O}_4$	<0.1
実施例3	$\text{Li}(\text{LiCr})_{0.10}\text{Mn}_{1.90}\text{O}_4$	<0.1
実施例4	$\text{Li}(\text{LiCr})_{0.30}\text{Mn}_{1.70}\text{O}_4$	<0.1
実施例5	$\text{Li}(\text{LiCr})_{0.50}\text{Mn}_{1.50}\text{O}_4$	<0.1
比較例5	$\text{Li}(\text{LiCr})_{0.80}\text{Mn}_{1.40}\text{O}_4$	5

\*

	正極活物質組成	初回電池容量に対する 100サイクル後の容量変化割合
実施例2	$\text{Li}(\text{LiCr})_{0.01}\text{Mn}_{1.99}\text{O}_4$	0.73
実施例3	$\text{Li}(\text{LiCr})_{0.10}\text{Mn}_{1.90}\text{O}_4$	0.78
実施例1	$\text{Li}(\text{LiCr})_{0.15}\text{Mn}_{1.85}\text{O}_4$	0.86
実施例4	$\text{Li}(\text{LiCr})_{0.30}\text{Mn}_{1.70}\text{O}_4$	0.87
実施例5	$\text{Li}(\text{LiCr})_{0.50}\text{Mn}_{1.50}\text{O}_4$	0.75
比較例1	$\text{LiLi}_{0.15}\text{Mn}_{1.85}\text{O}_4$	0.69
比較例2	$\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$	0.68
比較例3	$\text{LiMn}_2\text{O}_4$	0.60

【0030】表3に示されるように、 $\text{LiMn}_2\text{O}_4$ よりも、LiもしくはCrのいずれかで元素置換したLi

\*【0027】全置換量 $a+b$ が0.01以下では、LiまたはCrのいずれか一方による置換を行った正極活物質程度のMn溶出抑制効果しか得られなかった。また、全置換量 $a+b$ が0.5より多い場合にも十分なMn溶出抑制効果が得られなかった。たとえば、全置換量 $a+b$ が0.6の場合には、合成した正極活物質中に $\text{Li}(\text{LiCr})_{0.6}\text{Mn}_{1.4}\text{O}_4$ とは異なる結晶相（異相）が生成していることがXRDから確認されている。つまり、目的とする $\text{Li}(\text{LiCr})_{0.5}\text{Mn}_{1.5}\text{O}_4$ が生成していない可能性がある。したがって、Mnの溶出は正極活物質からのものでなく、異相からのものとも考えられるが、異相を含むことは、電池におけるエネルギー密度を低下させる原因となるので、正極活物質が異相を含まない単相材料であることが好ましいことはいうまでもない。

【0028】（電池のサイクル試験）前述した表1および表2に記した正極活物質中、Mnの溶出抑制効果が認められた全置換量 $a+b$ が0.01～0.5の範囲の $\text{Li}(\text{LiCr})_{0.15}\text{Mn}_{1.85}\text{O}_4$ 、および比較のために作製した $\text{LiLi}_{0.15}\text{Mn}_{1.85}\text{O}_4$ 、 $\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ 、 $\text{LiMn}_2\text{O}_4$ を用いた電池における充放電サイクル試験の結果を表3に示す。ここで、サイクル試験は、Mn溶出量を調べるための前述した充放電試験と同じ条件で行い、100回目の放電容量を、初回の放電容量で除した割合（容量変化割合）で示している。したがって、この値が大きいほど、サイクル特性が良好で劣化が小さいこととなる。

【0029】

【表3】

$\text{Li}_{0.15}\text{Mn}_{1.85}\text{O}_4$ や $\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ でサイクル特性の向上がみられるが、これらに対し、さらに、

LiおよびCrの2元素により同時置換した場合に、容量低下の少ない良好なサイクル特性が得られており、特に、全置換量 $a+b$ が、 $0.15 \leq a+b \leq 0.3$ の範囲において劣化の抑制効果が大きいことがわかる。

【0031】

【発明の効果】 上述の通り、本発明のリチウム二次電池によれば、 $\text{LiMn}_2\text{O}_4$ のMnの一部を、Liおよび\*

\*Crの2元素による同時置換した正極活物質が用いられているため、正極活物質中のMnの非水電解液への溶出が抑制されると同時に、充放電に伴う正極活物質の結晶構造の可逆性が改善され、その結果、充放電サイクル特性が改善され、しかも電池容量の低下が抑制されるという優れた効果が得られる。

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フロントページの続き

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AT

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION  
TECHNICAL PROBLEM MEANS EXAMPLE

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CLAIMS

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[Claim(s)]

[Claim 1] The lithium secondary battery characterized by using  $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$  (however, a expressing the amount of Li substitution and b expressing the amount of Cr substitution.) which carried out simultaneous substitution of a part of Mn of  $2\text{O}\text{LiMn}_4$  spinel by two elements of Li and Cr as a positive active material.

[Claim 2] The lithium secondary battery according to claim 1 with which the amounts a and b of substitution concerned are characterized by satisfying the relation of  $0.01 \leq a+b \leq 0.5$ ,  $a \neq 0$ , and  $b \neq 0$ .

[Claim 3] The lithium secondary battery according to claim 2 with which the amounts a and b of substitution concerned are characterized by satisfying the relation of  $0.15 \leq a+b \leq 0.3$ ,  $a \neq 0$ , and  $b \neq 0$ .

[Claim 4] A lithium secondary battery given in any 1 term of the claims 1-3 which the  $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$  concerned calcinate the salt of each element adjusted to the predetermined ratio, and/or the mixture of an oxide over 5 hours - 50 hours an oxidizing atmosphere and in 700 degrees C - 900 degrees C, and are characterized by being obtained.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the lithium secondary battery with a good charge-and-discharge cycle property using the lithium transition-metals multiple oxide as a positive active material in the rechargeable battery used as motorised power supplies, such as an operation power supply of carried type electronic equipment, an electric vehicle, or a hybrid electric vehicle.

[0002]

[Description of the Prior Art] Small lightweight-ization of carried type electronic equipment, such as a cellular phone, VTR, and a note type computer, is advancing at an increasing tempo in recent years, and the rechargeable battery which used for the negative-electrode active material the organic electrolytic solution which dissolved carbonaceous material in the electrolytic solution and dissolved Li ion electrolyte for the lithium multiple oxide in the organic solvent at the positive active material is increasingly used as the cell for power supplies.

[0003] Generally such a cell is called the lithium secondary battery or the lithium ion battery, and attention is attracted also as a motorised power supply of an achieving [ spread general / as an eco-friendly car / positive ]-not only against the background of aforementioned carrying type electronic equipment with large and energy density since cell voltage also has high feature with about about 4v but against the background of latest environmental problem electric vehicle, or a hybrid electric vehicle.

[0004] In such a lithium secondary battery, the cell capacity and a charge-and-discharge cycle property (henceforth a "cycle property") have a large place depending on the material property of the positive active material to be used. As a lithium transition-metals multiple oxide as a positive active material, concretely, although LiCoO<sub>2</sub> and the LiMn<sub>2</sub>O<sub>4</sub> grade are used, the production ground of Co is restricted about LiCoO<sub>2</sub>, and there is a problem in quantity of output never being able to say many, but using for a general-purpose lithium secondary battery, since it is expensive. Moreover, there is also a problem that power density is small, as compared with LiMn<sub>2</sub>O<sub>4</sub>.

[0005] On the other hand, LiMn<sub>2</sub>O<sub>4</sub> has a cheap raw material, and its power density is large, and it has the feature that potential is high. However, when LiMn<sub>2</sub>O<sub>4</sub> is used as a positive active material, in connection with the repeat of a charge-and-discharge cycle, service capacity falls gradually, and there is a problem that a good cycle property is not acquired. This is considered to be because it to change in [ the crystal structure ] irreversible by insertion and desorption of Li<sup>+</sup>.

[0006] Then, in order to improve the reversibility of this crystal structure, it is got blocked, the report that the thing which is made for other elements to dissolve and which replace a part of Mn by other one elements is effective is carried out to the skeleton of LiMn<sub>2</sub>O<sub>4</sub>, and the element substitution by the same + trivalent ion as Mn<sup>3+</sup>, for example, Co, Fe, Cr, etc., is considered.

[0007]

[Problem(s) to be Solved by the Invention] By performing element substitution by such + trivalent ion, it is a fact that a cycle property improves rather than element substitution before, therefore it is thought that the reversible improvement of the crystal structure accompanying insertion and desorption of Li<sup>+</sup> is achieved. However, even if artificers were the cases where such a spinel that carried out element substitution was used as a positive-electrode material, when cycle operation was performed, elution of Mn to the inside of the nonaqueous electrolyte used as the electrolytic solution took place with time, and they thought that elution of this Mn also caused [ of positive-electrode capacity (cell capacity) ] a fall, and a cycle property fell [ elution ].

[0008] Therefore, in order to raise the cycle property of a cell, it is desirable it not only to have the crystal structure which has the flexibility to insertion and desorption of Li<sup>+</sup>, but to use the spinel by which chemical reactivity with nonaqueous electrolyte was suppressed simultaneously, and the spinel to which elution of Mn does not take place at all preferably as a positive active material.

[0009]

[Means for Solving the Problem] this invention is made in view of the trouble of the conventional technology

mentioned above. That is, lithium secondary battery \*\* characterized by using  $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$  (however, a expressing the amount of Li substitution and b expressing the amount of Cr substitution.) which carried out simultaneous substitution of a part of Mn of  $2\text{OLiMn}_4$  spinel by two elements of Li and Cr according to this invention as a positive active material is offered.

[0010] Here, as for the amount a of Li substitution, and the amount b of Cr substitution, it is desirable to have satisfied simultaneously the relation of  $0.01 \leq a+b \leq 0.5$ ,  $a \neq 0$ , and  $b \neq 0$  \*\*. Moreover, it is still more desirable that the amounts a and b of substitution are in the range of  $0.15 \leq a+b \leq 0.3$ ,  $a \neq 0$ , and  $b \neq 0$  \*\*. In addition, this composition of  $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$  is suitably performed by being an oxidizing atmosphere and the range of 700 degrees C - 900 degrees C, and calcinating the salt of each element adjusted to the predetermined ratio, and/or the mixture of an oxide over 5 hours - 50 hours.

[0011]

[Embodiments of the Invention] Also by suppressing the elution to the nonaqueous electrolyte of Mn at the same time it improves the reversibility of the crystal structure over insertion and desorption of  $\text{Li}^+$  and raises a cycle property in the lithium secondary battery of this invention  $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$  which carried out simultaneous substitution of a part of Mn of  $2\text{OLiMn}_4$  spinel by two elements of Li and Cr in order to suppress the fall of positive-electrode capacity and to raise a cycle property (however, a expresses the amount of Li substitution and b expresses the amount of Cr substitution.) It uses as a positive active material.

[0012] The whole amount (henceforth "total amount of substitution")  $a+b$  of substitution is made into the range of  $0.01 \leq a+b \leq 0.5$ , and each amounts a and b of substitution of Li and Cr need to fulfill simultaneously the conditions of  $a \neq 0$  and  $b \neq 0$  here. That is, in order to suppress the elution to the nonaqueous electrolyte of Mn, even if the simultaneous substitution which made two elements of Li and Cr the couple is required and one of elements is missing, the effect of suppressing Mn elution cannot be demonstrated. And when all amount  $a+b$  of substitution is in the range of  $0.15 \leq a+b \leq 0.3$ , as shown in the example mentioned later, the elution depressor effect of Mn is demonstrated most and a good cycle property is acquired.

[0013] In addition, improvement in a cycle property does not appear [ all amount  $a+b$  of substitution ] or less in 0.01, and the effect of simultaneous substitution is not accepted. On the other hand, by 0.5 \*\*, generation of an unusual appearance is accepted for all amount  $a+b$  of substitution by powder X-ray diffractometry (XRD) in material composition, namely, the single phase matter is not obtained. Since such an unusual appearance does not contribute to a cell reaction only by increasing the weight of a positive active material, it cannot be overemphasized by that the generation must be avoided.

[0014] By using  $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$  mentioned above as a positive active material, the reversible improvement of the crystal structure to insertion and desorption of  $\text{Li}^+$  and suppression of the elution to the nonaqueous electrolyte of Mn are achieved simultaneously, and fast improvement in a cycle property is achieved. When it uses as a power supply for motorised of an electric vehicle or a hybrid electric vehicle, especially the improvement in such a cycle property is very important, in order to maintain performance-traverse ability, such as a predetermined acceleration performance and a climb performance, and to maintain the continuation mileage per 1 charge.

[0015] Production of  $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$  is performed by being an oxidizing atmosphere and the range of 700 degrees C - 900 degrees C, and calcinating the salt of each element adjusted to the predetermined ratio as a raw material, and/or the mixture of an oxide over 5 hours - 50 hours, and a single-phase product can be obtained in this way.

[0016] Here, although it is desirable that especially the salt of each element uses a temperature up, the carbonate which cracked gas detrimental at the time of baking does not generate, and acetate to say nothing of it being desirable that what has it can be used although not limited, a nitrate, a hydrochloride, a sulfate, etc. can also be used. [ high purity and cheap as a raw material, ]

[0017] Now, especially the other materials used in production of a cell are not limited, and well-known various material can be conventionally used for them. For example, as a negative-electrode active material, carbonaceous material, such as artificial graphites, such as amorphous system carbonaceous material, such as soft carbon and a hard carbon, and high graphitized-carbon material, or a natural graphite, can be used.

[0018] Moreover, as the organic electrolytic solution, what dissolved one kind or two kinds or more is suitably used for the independent solvent or mixed solvents of an organic solvent, such as a thing of carbonate systems, such as ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC), propylene carbonate (PC) and gamma-butyrolactone, a tetrahydrofuran, and an acetonitrile, in the lithium complex fluorine compound of  $\text{LiPF}_6$  as an electrolyte, or  $\text{LiBF}_4$  grade, or a lithium halogenide called  $\text{LiClO}_4$ .

[0019]

[Example] Hereafter, this invention is explained to an example still in detail based on an experimental result.

[0020] (Manufacture of positive-active-material  $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$ ) it becomes various kinds of composition shown in the left column of Table 1, using each powder of commercial  $\text{Li}_2\text{CO}_3$ , and  $\text{MnO}_2$  and Cr

2O<sub>3</sub> as a start raw material -- as -- weighing capacity -- it mixed, and calcinated at an oxidizing atmosphere and 800 degrees C for 24 hours, and the positive active material was compounded Here, the material which replaced a part of Mn only by Li or Cr for comparison, and LiMn 2O<sub>4</sub> which does not perform substitution were also compounded. In addition, except for LiMn 2O<sub>4</sub> which does not perform element substitution, all amount a+b of substitution of all was set to 0.15.

[0021]

[Table 1]

	正極活物質組成	Mn量(10 <sup>-3</sup> mol/L)
実施例1	Li(LiCr) <sub>0.15</sub> Mn <sub>1.85</sub> O <sub>4</sub>	<0.1
比較例1	LiLi <sub>0.15</sub> Mn <sub>1.85</sub> O <sub>4</sub>	4
比較例2	LiCr <sub>0.15</sub> Mn <sub>1.85</sub> O <sub>4</sub>	3
比較例3	LiMn <sub>2</sub> O <sub>4</sub>	12

[0022] (Manufacture of a cell) First, about each of the various positive active materials which carried out as above-mentioned and were produced, the binding material slack polyvinylidene fluoride was mixed with a positive active material and electric conduction material slack acetylene black powder by the ratio of 50:2:3 by the weight ratio, and positive-electrode material was produced. Press forming of the 0.02g of the positive-electrode material was carried out to disc-like [ with a diameter / phi / of 20mm ] by the pressure of 300 kg/cm<sup>2</sup>, and it considered as the positive electrode. In this way, the coin cell was produced using the electrolytic solution which dissolved LiPF<sub>6</sub> as an electrolyte in the produced positive electrode and the organic solvent mixed by volume ratios [ diethyl carbonate / ethylene carbonate, ] at a rate which becomes 1 mol/L, and the separator which separates the negative electrode which consists of carbon, and a positive electrode and a negative electrode.

[0023] (Measurement of the elution volume to the inside of the nonaqueous electrolyte of a positive active material) According to the capacity of a positive active material, it is the constant-current-constant voltage of 1C rate about the produced coin cell, and is 4.1V. It charged, and after extracting nonaqueous electrolyte from the coin cell after 100 cycle \*\*\*\*\* and diluting with distilled water the charge and discharge test made to discharge to 2.5V by the constant current of 1C rate similarly 100 times, the amount of Mn contained in nonaqueous electrolyte was analyzed using inductive-coupling RF plasma luminescence equipment (ICP). Since Mn is not contained in the nonaqueous electrolyte at the time of cell manufacture, the degree of elution of Mn from a positive active material can be known by this analysis.

[0024] The measurement result of ICP is described in the right column of Table 1. as compared with LiMn 2O<sub>4</sub> which does not perform element substitution, the elution volume of Mn is stopped by about 1 / three to 1/4 by what performed substitution by either Li or Cr -- \*\*\*\* -- although it has stopped, from Li(LiCr)<sub>0.15</sub>Mn<sub>1.85</sub>O<sub>4</sub> of this invention which performed simultaneous substitution by two elements of Li and Cr, it turns out that elution of Mn is suppressed almost completely That is, in order to suppress elution of Mn, the substitution by either [ of Mn ] Li or Cr is inadequate, and the simultaneous substitution by two elements of Li and Cr enabled it to suppress elution of Mn for the first time nearly completely.

[0025] Next, in the simultaneous substitution by two elements of Li and Cr, the range of all amount a+b of substitution from which Mn elution depressor effect is obtained was investigated. Composition of the compound positive active material and the measurement result of Mn elution volume by the analysis using ICP mentioned above are shown in Table 2.

[0026]

[Table 2]

	正極活物質組成	Mn量(10 <sup>-3</sup> mol/L)
比較例4	Li(LiCr) <sub>0.008</sub> Mn <sub>1.992</sub> O <sub>4</sub>	3
実施例2	Li(LiCr) <sub>0.01</sub> Mn <sub>1.99</sub> O <sub>4</sub>	<0.1
実施例3	Li(LiCr) <sub>0.10</sub> Mn <sub>1.90</sub> O <sub>4</sub>	<0.1
実施例4	Li(LiCr) <sub>0.30</sub> Mn <sub>1.70</sub> O <sub>4</sub>	<0.1
実施例5	Li(LiCr) <sub>0.50</sub> Mn <sub>1.50</sub> O <sub>4</sub>	<0.1
比較例5	Li(LiCr) <sub>0.60</sub> Mn <sub>1.40</sub> O <sub>4</sub>	5

[0027] Only Mn elution depressor effect about a positive active material to which all amount a+b of substitution performed substitution by either Li or Cr or less by 0.01 was obtained. Moreover, when there was more all amount a+b of substitution than 0.5, sufficient Mn elution depressor effect was not obtained. For example, when all amount a+b of substitution is 0.6, it is checked from XRD that a crystal phase (unusual appearance) which is different in Li (LiCr<sub>b</sub>) Mn<sub>2-(a+b)</sub> O<sub>4</sub> in the compound positive active material is generating. That is, target Li(LiCr)<sub>0.6</sub>Mn<sub>1.4</sub>O<sub>4</sub> may not be generating. Therefore, although elution of Mn is considered to be also a thing from an unusual appearance instead of the thing from a positive active material, since it becomes the cause of reducing the energy

density in a cell, it cannot be overemphasized by that it is desirable that it is the single phase material in which a positive active material does not contain an unusual appearance that an unusual appearance is included.

[0028] (Cycle examination of a cell) The result of the charge-and-discharge cycle examination in the cell using  $\text{LiLi}_{0.15}\text{Mn}_{1.85}\text{O}_4$  which all amount a+b of substitution in which the elution depressor effect of Mn was accepted produced for  $\text{Li}(\text{LiCr})_{a+b}\text{Mn}_{2-(a+b)}\text{O}_4$  of the range of 0.01-0.5 and comparison,  $\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ , and  $\text{LiMn}_2\text{O}_4$  is shown in Table 3 among the positive active material described in Table 1 and 2 mentioned above. Here, the rate (capacity change rate) which performed the cycle examination on the same conditions as the charge and discharge test mentioned above for investigating Mn elution volume, and  $\Delta$ (ed) 100th service capacity by first-time service capacity shows. Therefore, a cycle property will be so good that this value is large, and degradation will be small.

[0029]

[Table 3]

	正極活物質組成	初回電池容量に対する 100サイクル後の容量変化割合
実施例2	$\text{Li}(\text{LiCr})_{0.01}\text{Mn}_{1.99}\text{O}_4$	0.73
実施例3	$\text{Li}(\text{LiCr})_{0.10}\text{Mn}_{1.90}\text{O}_4$	0.78
実施例1	$\text{Li}(\text{LiCr})_{0.15}\text{Mn}_{1.85}\text{O}_4$	0.86
実施例4	$\text{Li}(\text{LiCr})_{0.30}\text{Mn}_{1.70}\text{O}_4$	0.87
実施例5	$\text{Li}(\text{LiCr})_{0.50}\text{Mn}_{1.50}\text{O}_4$	0.75
比較例1	$\text{LiLi}_{0.15}\text{Mn}_{1.85}\text{O}_4$	0.69
比較例2	$\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$	0.68
比較例3	$\text{LiMn}_2\text{O}_4$	0.60

[0030] Although improvement in a cycle property is found rather than  $\text{LiMn}_2\text{O}_4$  from  $\text{LiLi}_{0.15}\text{Mn}_{1.85}\text{O}_4$  and  $\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$  which carried out element substitution by either Li or Cr as shown in Table 3 When simultaneous substitution is further carried out with two elements of Li and Cr to these, the good cycle property with few capacity falls is acquired, and it turns out especially that all amount a+b of substitution of the depressor effect of degradation is large in the range of  $0.15 \leq a+b \leq 0.3$ .

[0031]

[Effect of the Invention] Since the positive active material by two elements of Li and Cr which carried out simultaneous substitution is used in a part of Mn of  $\text{LiMn}_2\text{O}_4$  according to the lithium secondary battery of this invention an above-mentioned passage, The reversibility of the crystal structure of the positive active material accompanying charge and discharge is improved, consequently a charge-and-discharge cycle property is improved, and the outstanding effect that the fall of cell capacity is moreover suppressed is acquired at the same time the elution to the nonaqueous electrolyte of Mn in a positive active material is suppressed.

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TECHNICAL FIELD

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[0004] In such a lithium secondary battery, the cell capacity and a charge-and-discharge cycle property (henceforth a "cycle property") have a large place depending on the material property of the positive active material to be used. As a lithium transition-metals multiple oxide as a positive active material, concretely, although LiCoO<sub>2</sub> and the LiMn<sub>2</sub>O<sub>4</sub> grade are used, the production ground of Co is restricted about LiCoO<sub>2</sub>, and there is a problem in quantity of output never being able to say many, but using for a general-purpose lithium secondary battery, since it is expensive. Moreover, there is also a problem that power density is small, as compared with LiMn<sub>2</sub>O<sub>4</sub>.

[0005] On the other hand, LiMn<sub>2</sub>O<sub>4</sub> has a cheap raw material, and its power density is large, and it has the feature that potential is high. However, when LiMn<sub>2</sub>O<sub>4</sub> is used as a positive active material, in connection with the repeat of a charge-and-discharge cycle, service capacity falls gradually, and there is a problem that a good cycle property is not acquired. This is considered to be because it to change in [ the crystal structure ] irreversible by insertion and desorption of Li<sup>+</sup>.

[0006] Then, in order to improve the reversibility of this crystal structure, it is got blocked, the report that the thing which is made for other elements to dissolve and which replace a part of Mn by other one elements is effective is carried out to the frame of LiMn<sub>2</sub>O<sub>4</sub>, and the element substitution by the same + trivalent ion as Mn<sup>3+</sup>, for example, Co, Fe, Cr, etc., is considered.

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EFFECT OF THE INVENTION

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[Effect of the Invention] Since the positive active material by two elements of Li and Cr which carried out simultaneous substitution is used in a part of Mn of  $\text{LiMn}_2\text{O}_4$  according to the lithium secondary battery of this invention an above-mentioned passage, The reversibility of the crystal structure of the positive active material accompanying charge and discharge is improved, consequently a charge-and-discharge cycle property is improved, and the outstanding effect that the fall of cell capacity is moreover suppressed is acquired at the same time the elution to the nonaqueous electrolyte of Mn in a positive active material is suppressed.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] By performing element substitution by such + trivalent ion, it is a fact that a cycle property improves rather than element substitution before, therefore it is thought that the reversible improvement of the crystal structure accompanying insertion and desorption of  $\text{Li}^+$  is achieved. However, even if artificers were the cases where such a spinel that carried out element substitution was used as a positive-electrode material, when cycle operation was performed, elution of Mn to the inside of the nonaqueous electrolyte used as the electrolytic solution took place with time, and they thought that elution of this Mn also caused [ of positive-electrode capacity (cell capacity) ] a fall, and a cycle property fell [ elution ].

[0008] Therefore, in order to raise the cycle property of a cell, it is desirable it not only to have the crystal structure which has the flexibility to insertion and desorption of  $\text{Li}^+$ , but to use the spinel by which chemical reactivity with nonaqueous electrolyte was suppressed simultaneously, and the spinel to which elution of Mn does not take place at all preferably as a positive active material.

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## MEANS

[Means for Solving the Problem] this invention is made in view of the trouble of the conventional technology mentioned above. That is, lithium secondary battery \*\* characterized by using  $\text{Li}(\text{Li}_{a\text{Cr}_b})\text{Mn}_{2-(a+b)}\text{O}_4$  (however, a expressing the amount of Li substitution and b expressing the amount of Cr substitution.) which carried out simultaneous substitution of a part of Mn of  $2\text{OLiMn}_4$  spinel by two elements of Li and Cr according to this invention as a positive active material is offered.

[0010] Here, as for the amount a of Li substitution, and the amount b of Cr substitution, it is desirable to have satisfied simultaneously the relation of  $0.01 \leq a+b \leq 0.5$ ,  $a \neq 0$ , and  $b \neq 0$  \*\*. Moreover, it is still more desirable that the amounts a and b of substitution are in the range of  $0.15 \leq a+b \leq 0.3$ ,  $a \neq 0$ , and  $b \neq 0$  \*\*. In addition, this composition of  $\text{Li}(\text{Li}_{a\text{Cr}_b})\text{Mn}_{2-(a+b)}\text{O}_4$  is suitably performed by being an oxidizing atmosphere and the range of 700 degrees C - 900 degrees C, and calcinating the salt of each element adjusted to the predetermined ratio, and/or the mixture of an oxide over 5 hours - 50 hours.

[0011]

[Embodiments of the Invention] Also by suppressing the elution to the nonaqueous electrolyte of Mn at the same time it improves the reversibility of the crystal structure over insertion and desorption of  $\text{Li}^+$  and raises a cycle property in the lithium secondary battery of this invention  $\text{Li}(\text{Li}_{a\text{Cr}_b})\text{Mn}_{2-(a+b)}\text{O}_4$  which carried out simultaneous substitution of a part of Mn of  $2\text{OLiMn}_4$  spinel by two elements of Li and Cr in order to suppress the fall of positive-electrode capacity and to raise a cycle property (however, a expresses the amount of Li substitution and b expresses the amount of Cr substitution.) It uses as a positive active material.

[0012] The whole amount (henceforth "total amount of substitution")  $a+b$  of substitution is made into the range of  $0.01 \leq a+b \leq 0.5$ , and each amounts a and b of substitution of Li and Cr need to fulfill simultaneously the conditions of  $a \neq 0$  and  $b \neq 0$  here. That is, in order to suppress the elution to the nonaqueous electrolyte of Mn, even if the simultaneous substitution which made two elements of Li and Cr the couple is required and one of elements is missing, the effect of suppressing Mn elution cannot be demonstrated. And when all amount  $a+b$  of substitution is in the range of  $0.15 \leq a+b \leq 0.3$ , as shown in the example mentioned later, the elution depressor effect of Mn is demonstrated most and a good cycle property is acquired.

[0013] In addition, improvement in a cycle property does not appear [ all amount  $a+b$  of substitution ] or less in 0.01, and the effect of simultaneous substitution is not accepted. On the other hand, by 0.5 \*\*, generation of an unusual appearance is accepted for all amount  $a+b$  of substitution by powder X-ray diffractometry (XRD) in material composition, namely, the single phase matter is not obtained. Since such an unusual appearance does not contribute to a cell reaction only by increasing the weight of a positive active material, it cannot be overemphasized by that the generation must be avoided.

[0014] By using  $\text{Li}(\text{Li}_{a\text{Cr}_b})\text{Mn}_{2-(a+b)}\text{O}_4$  mentioned above as a positive active material, the reversible improvement of the crystal structure to insertion and desorption of  $\text{Li}^+$  and suppression of the elution to the nonaqueous electrolyte of Mn are achieved simultaneously, and fast improvement in a cycle property is achieved. When it uses as a power supply for motorised of an electric vehicle or a hybrid electric vehicle, especially the improvement in such a cycle property is very important, in order to maintain performance-traverse ability, such as a predetermined acceleration performance and a climb performance, and to maintain the continuation mileage per 1 charge.

[0015] Production of  $\text{Li}(\text{Li}_{a\text{Cr}_b})\text{Mn}_{2-(a+b)}\text{O}_4$  is performed by being an oxidizing atmosphere and the range of 700 degrees C - 900 degrees C, and calcinating the salt of each element adjusted to the predetermined ratio as a raw material, and/or the mixture of an oxide over 5 hours - 50 hours, and a single-phase product can be obtained in this way.

[0016] Here, although it is desirable that especially the salt of each element uses a temperature up, the carbonate which cracked gas detrimental at the time of baking does not generate, and acetate to say nothing of it being desirable that what has it can be used although not limited, a nitrate, a hydrochloride, a sulfate, etc. can also be used. [ high purity and cheap as a raw material, ]

[0017] Now, especially the other materials used in production of a cell are not limited, and well-known various material can be conventionally used for them. For example, as a negative-electrode active material, carbonaceous material, such as artificial graphites, such as amorphous system carbonaceous material, such as soft carbon and a hard carbon, and high graphitized-carbon material, or a natural graphite, can be used.

[0018] Moreover, as the organic electrolytic solution, what dissolved one kind or two kinds or more is suitably used for the independent solvent or mixed solvents of an organic solvent, such as a thing of carbonate systems, such as ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC), propylene carbonate (PC) and gamma-butyrolactone, a tetrahydrofuran, and an acetonitrile, in the lithium complex fluorine compound of  $\text{LiPF}_6$  as an electrolyte, or  $\text{LiBF}_4$  grade, or a lithium halogenide called  $\text{LiClO}_4$ .

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## EXAMPLE

[Example] Hereafter, this invention is explained to an example still in detail based on an experimental result.

[0020] (Manufacture of positive-active-material  $\text{Li}(\text{Li}_a\text{Cr}_b)\text{Mn}_{2-(a+b)}\text{O}_4$ ) it becomes various kinds of composition shown in the left column of Table 1, using each powder of commercial  $\text{Li}_2\text{CO}_3$ , and  $\text{MnO}_2$  and  $\text{Cr}_2\text{O}_3$  as a start raw material -- as -- weighing capacity -- it mixed, and calcinated at an oxidizing atmosphere and 800 degrees C for 24 hours, and the positive active material was compounded Here, the material which replaced a part of Mn only by Li or Cr for comparison, and  $\text{LiMn}_2\text{O}_4$  which does not perform substitution were also compounded. In addition, except for  $\text{LiMn}_2\text{O}_4$  which does not perform element substitution, all amount a+b of substitution of all was set to 0.15.

[0021]

[Table 1]

	正極活物質組成	Mn量( $10^{-3}\text{mol/L}$ )
実施例1	$\text{Li}(\text{LiCr})_{0.15}\text{Mn}_{1.85}\text{O}_4$	<0.1
比較例1	$\text{LiLi}_{0.15}\text{Mn}_{1.85}\text{O}_4$	4
比較例2	$\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$	3
比較例3	$\text{LiMn}_2\text{O}_4$	12

[0022] (Manufacture of a cell) First, about each of the various positive active materials which carried out as above-mentioned and were produced, the binding material slack polyvinylidene fluoride was mixed with a positive active material and electric conduction material slack acetylene black powder by the ratio of 50:2:3 by the weight ratio, and positive-electrode material was produced. Press forming of the 0.02g of the positive-electrode material was carried out to disc-like [ with a diameter /  $\phi$  / of 20mm ] by the pressure of 300 kg/cm<sup>2</sup>, and it considered as the positive electrode. In this way, the coin cell was produced using the electrolytic solution which dissolved  $\text{LiPF}_6$  as an electrolyte in the produced positive electrode and the organic solvent mixed by volume ratios [ diethyl carbonate / ethylene carbonate, ] at a rate which becomes 1 mol/L, and the separator which separates the negative electrode which consists of carbon, and a positive electrode and a negative electrode.

[0023] (Measurement of the elution volume to the inside of the nonaqueous electrolyte of a positive active material) According to the capacity of a positive active material, it is the constant-current-constant voltage of 1C rate about the produced coin cell, and is 4.1V. It charged, and after extracting nonaqueous electrolyte from the coin cell after 100 cycle \*\*\*\*\* and diluting with distilled water the charge and discharge test made to discharge to 2.5V by the constant current of 1C rate similarly 100 times, the amount of Mn contained in nonaqueous electrolyte was analyzed using inductive-coupling RF plasma luminescence equipment (ICP). Since Mn is not contained in the nonaqueous electrolyte at the time of cell manufacture, the degree of elution of Mn from a positive active material can be known by this analysis.

[0024] The measurement result of ICP is described in the right column of Table 1. as compared with  $\text{LiMn}_2\text{O}_4$  which does not perform element substitution, the elution volume of Mn is stopped by about 1 / three to 1/4 by what performed substitution by either Li or Cr -- \*\*\*\* -- although it has stopped, from  $\text{Li}(\text{LiCr})_{0.15}\text{Mn}_{1.85}\text{O}_4$  of this invention which performed simultaneous substitution by two elements of Li and Cr, it turns out that elution of Mn is suppressed almost completely That is, in order to suppress elution of Mn, the substitution by either [ of Mn ] Li or Cr is inadequate, and the simultaneous substitution by two elements of Li and Cr enabled it to suppress elution of Mn for the first time nearly completely.

[0025] Next, in the simultaneous substitution by two elements of Li and Cr, the range of all amount a+b of substitution from which Mn elution depressor effect is obtained was investigated. Composition of the compound positive active material and the measurement result of Mn elution volume by the analysis using ICP mentioned above are shown in Table 2.

[0026]

[Table 2]

	正極活物質組成	Mn量( $10^{-3}$ mol/L)
比較例4	Li(LiCr) <sub>0.008</sub> Mn <sub>1.992</sub> O <sub>4</sub>	3
実施例2	Li(LiCr) <sub>0.01</sub> Mn <sub>1.99</sub> O <sub>4</sub>	<0.1
実施例3	Li(LiCr) <sub>0.10</sub> Mn <sub>1.90</sub> O <sub>4</sub>	<0.1
実施例4	Li(LiCr) <sub>0.30</sub> Mn <sub>1.70</sub> O <sub>4</sub>	<0.1
実施例5	Li(LiCr) <sub>0.50</sub> Mn <sub>1.50</sub> O <sub>4</sub>	<0.1
比較例5	Li(LiCr) <sub>0.60</sub> Mn <sub>1.40</sub> O <sub>4</sub>	5

[0027] Only Mn elution depressor effect about a positive active material to which all amount a+b of substitution performed substitution by either Li or Cr or less by 0.01 was obtained. Moreover, when there was more all amount a+b of substitution than 0.5, sufficient Mn elution depressor effect was not obtained. For example, when all amount a+b of substitution is 0.6, it is checked from XRD that a crystal phase (unusual appearance) which is different in Li (Li<sub>a</sub>Cr<sub>b</sub>) Mn<sub>2</sub>-(a+b) O<sub>4</sub> in the compound positive active material is generating. That is, target Li(LiCr)<sub>0.6</sub>Mn<sub>1.4</sub>O<sub>4</sub> may not be generating. Therefore, although elution of Mn is considered to be also a thing from an unusual appearance instead of the thing from a positive active material, since it becomes the cause of reducing the energy density in a cell, it cannot be overemphasized by that it is desirable that it is the single phase material in which a positive active material does not contain an unusual appearance that an unusual appearance is included.

[0028] (Cycle examination of a cell) The result of the charge-and-discharge cycle examination in the cell using LiLi<sub>0.15</sub>Mn<sub>1.85</sub>O<sub>4</sub> which all amount a+b of substitution in which the elution depressor effect of Mn was accepted produced for Li(LiCr)<sub>a</sub>bMn<sub>2</sub>-(a+b) O<sub>4</sub> of the range of 0.01-0.5 and comparison, LiCr<sub>0.15</sub>Mn<sub>1.85</sub>O<sub>4</sub>, and LiMn<sub>2</sub>O<sub>4</sub> is shown in Table 3 among the positive active material described in Table 1 and 2 mentioned above. Here, the rate (capacity change rate) which performed the cycle examination on the same conditions as the charge and discharge test mentioned above for investigating Mn elution volume, and \*(ed) 100th service capacity by first-time service capacity shows. Therefore, a cycle property will be so good that this value is large, and degradation will be small.

[0029]

[Table 3]

	正極活物質組成	初回電池容量に対する 100サイクル後の容量変化割合
実施例2	Li(LiCr) <sub>0.01</sub> Mn <sub>1.99</sub> O <sub>4</sub>	0.73
実施例3	Li(LiCr) <sub>0.10</sub> Mn <sub>1.90</sub> O <sub>4</sub>	0.78
実施例1	Li(LiCr) <sub>0.15</sub> Mn <sub>1.85</sub> O <sub>4</sub>	0.86
実施例4	Li(LiCr) <sub>0.30</sub> Mn <sub>1.70</sub> O <sub>4</sub>	0.87
実施例5	Li(LiCr) <sub>0.50</sub> Mn <sub>1.50</sub> O <sub>4</sub>	0.75
比較例1	LiLi <sub>0.15</sub> Mn <sub>1.85</sub> O <sub>4</sub>	0.69
比較例2	LiCr <sub>0.15</sub> Mn <sub>1.85</sub> O <sub>4</sub>	0.68
比較例3	LiMn <sub>2</sub> O <sub>4</sub>	0.60

[0030] Although improvement in a cycle property is found rather than LiMn<sub>2</sub>O<sub>4</sub> from LiLi<sub>0.15</sub>Mn<sub>1.85</sub>O<sub>4</sub> and LiCr<sub>0.15</sub>Mn<sub>1.85</sub>O<sub>4</sub> which carried out element substitution by either Li or Cr as shown in Table 3 When simultaneous substitution is further carried out with two elements of Li and Cr to these, the good cycle property with few capacity falls is acquired, and it turns out especially that all amount a+b of substitution of the depressor effect of degradation is large in the range of  $0.15 \leq a+b \leq 0.3$ .

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